

**Remarks**

The Examiner stated that the information disclosure statement filed 12/08/2004 did not comply with 37 CFR 1.98(a)(2) with respect to GB834,376 and JP 48013399A (abstract) because a legible copy was not provided. Applicants apologize if the copies were not legible and have included new copies with this response in the appendix.

Claims 1-8 and 10-18 are pending in this case. Claims 1, 12 and 13 have been amended and Claim 9 has been cancelled. The Examiner rejected claims 1-14 and 16-18 under 35 U.S.C. §103(a) as being unpatentable over Kurita et al (US4,985,286). The Examiner also rejected Claim 15 under 35 U.S.C. §103(a) as being unpatentable over Kurita et al (US4,985,286) in view of Amidaiji et al (US6,451, 437).

Applicants have amended Claims 1 and 13 to include the limitation described in Claim 9 where the amount of Component C in the composition is equal to or greater than the amount of Component B. Applicants believe that this amendment should overcome the examiner's rejections of any of the claims under 35 U.S.C. §103(a). Both Kurita and Amidaiji's compositions are different from the present invention. While both Kurita and Amidaiji utilize a metal alkoxide in their compositions – it is described and used as a catalyst and therefore only small amounts are used. For example, column 8, lines 23-32 of Kurita describes the amount of catalyst added which is generally from 0.01 to 7 parts by weight per 100 parts by weight of component (A) and further states "...if the curing catalyst is used in an amount exceeding 7 parts by weight, there is a drawback that such a large amount of catalyst impairs the storage stability of the abrasion-concealing agent..." In addition, Amidaiji also provides in column 15, lines 37-42 that the catalyst is used in an amount not greater than 10 parts by weight per 100 parts by weight of component (A). Applicants invention requires that the present invention comprises among other ingredients, 10 to 150 parts by weight of at least one metal alkoxide. Further, as described above, Applicants have amended Claims 1 and 13 to include the limitation described in Claim 9 so the amount of Component C in the composition (or used to make the composition) is equal to or greater than the amount of Component B. This is very different from Kurita or Amidaiji. In



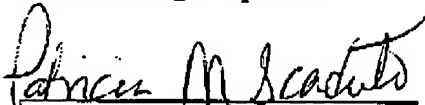
particular, Kurita teaches away from this by stating amounts larger than 7 parts by weight would impair storage stability. A review of Tables 2 and 4 of the present specification illustrates that the present invention has improved stability when Component (C) is equal to or larger than Component (B).

For the reasons described above, Applicants submit that claims 1-14 and 16-18 are not obvious over Kurita et al (US4,985,286) and Claim 15 is not obvious over Kurita et al (US4,985,286) in view of Amidaiji et al (US6,451, 437). Applicants respectfully request that the Examiner reconsider the above rejections and allow the amended claims to issue.

This reply is being submitted within the period for response to the outstanding office action. Although the applicants believe in good faith that no extensions of time are needed, the applicants hereby petition for any necessary extensions of time. You are authorized to charge deposit account 04-1520 for any fees necessary to maintain the pendency of this application. You are authorized to make any additional copies of this sheet needed to accomplish the purposes provided for herein and to charge any fee for such copies to deposit account 04-1520.

Respectfully Submitted,

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APPENDIX

See attached copy of GB834,376 – 8 pages  
And the abstract of JP48013399A – 1 page



DIALOG(R) File 351:Derwent WPI  
(c) 2004 Thomson Derwent. All rts. reserv.

AA- 1973-47712U/ 197334 |  
TI- Soil-resistant finishing - for fibre prods|  
PA- KANEGAFUCHI CO LTD (KANE )|  
NC- 001|  
NP- 001|  
PN- JP 48001399 A  
AN- <PR> JP 7134944 A 19710522| 197334 B|  
AB- <BASIC> JP 48001399 A  
An emulsion contg. Me H silicone and Na trichloroacetate was applied to a fabric and steam-heated to improved the soil resistance of the fabric. Thus, 60 parts trimethylsilane terminated Me H silicone with d.p. 22 was dispersed in 34 pts. water contg. 4 pts of a cationic surfactant, and 3 pts of the emulsion was mixed with 2 pts.  $\text{CCl}_3\text{CO}_2\text{Na}$  and 95 pts. water. A nylon carpet was sprayed with the mixt. to 5% dry pickup, steam heated 30 min at 100 degrees and dried 20 min at 60 degrees. The carpet had improved soil resistance over that of a similar carpet treated similarly but dry heated 3 min at 140 degrees.|  
DE- <TITLE TERMS> SOIL; RESISTANCE; FINISH; FIBRE; PRODUCT|  
DC- A87; F06|  
MC- <CPI> A06-A00E1; A12-G03; A12-S05M; F03-C02|  
FS- CPI||



## PATENT SPECIFICATION

NO DRAWINGS

834376



Date of Application and filing Complete Specification: April 1, 1958.

No. 10413/58.

Application made in United States of America on May 13, 1957.

Complete Specification Published: May 4, 1960.

Index at acceptance:—Classes 2(7), T6B; and 140, P3(E: F2: G2: G4).

International Classification:—C08g, D01fm.

## COMPLETE SPECIFICATION

## Improvements relating to Organopolysiloxane Water-Repellent Compositions

We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1, River Road, Schenectady, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to water-repellent organopolysiloxanes useful in rendering various porous materials water-repellent without the necessity of using heat to bring out the optimum water-repellency of the treated surface.

The invention consists in a composition comprising, by weight, (1) from 10 to 60 per cent of an orthotitanate having the general formula  $Ti(OR)_4$ , where each R is an aliphatic hydrocarbon radical of less than twelve carbon atoms or an hydroxylated or aminated aliphatic hydrocarbon radical of less than twelve carbon atoms and containing less than four hydroxy radicals, or an aliphatic hydrocarbon-soluble partial hydrolyzate thereof, (2) from 25 to 75 per cent of a methylpolysiloxane copolymer consisting essentially of trimethylsiloxy units and  $SiO_2$  units wherein said units are in such proportion that the ratio of methyl radicals to silicon atoms ranges from about 1 to 1.25 methyl radicals per silicon atom, and (3) from 10 to 50 per cent of a liquid organopolysiloxane having the formula  $R_1^nSiO_{2-n}$  where the  $R_1$ 's represent both lower

alkyl (e.g., methyl and ethyl) radicals and chlorinated phenyl radicals in which the chlorinated phenyl radicals contain an average of from 3 to 5 chlorine atoms per phenyl nucleus, and the chlorinated phenyl radicals constitute from 5 to 25 per cent of the total number of lower alkyl and chlorophenyl radicals; and  $n$  has an average value above 1.96 but below 2.5, the lower alkyl chloro-

phenylpolysiloxane liquid having a viscosity of from 10 to 100,000 centistokes, e.g., from 15 to 5,000 centistokes, when measured at 25° C.

Various means have been employed in the past to impart water-repellency to textiles employing organopolysiloxanes for the purpose. This treatment has usually involved using methyl hydrogen polysiloxanes, together with catalysts such as lead octoate and tin naphthenate which convert these methyl hydrogen polysiloxanes to the cross-linked state. In general, such conversion requires the application of elevated temperatures, for instance, from 150° to 200° C. for varying lengths of time in order to obtain an optimum degree of water-repellency. The use of methyl hydrogen polysiloxanes for this purpose is disclosed in Specification No. 705,277.

The type of applications described above have been generally successful on a commercial scale when employed in textile mills during fabric finishing operations. However, this technology is not applicable to a consumer product application because the methyl hydrogen polysiloxane is usually not stable for a sufficient length of time in the presence of catalysts to render it usable on a small scale home use. Moreover, the requirement of a heating cycle to bring out the optimum cure and water-repellency is obviously not practical for home applications because of the lack of adequate facilities, including means for applying the water-repellent.

We have now discovered that a specific combination of ingredients composed of a mixture of the aforesaid organotitanate, a methylpolysiloxane polymer, and an alkyl-chlorophenylpolysiloxane polymer can be readily applied to porous surfaces, particularly textile surfaces, such as cotton, by convenient means, such as from an aerosol pressure container, and the treated surface is readily converted to a highly water-repellent state without the necessity of using heat to bring out



the optimum degree of water-repellency. Moreover, the mixture of ingredients used is stable indefinitely, and requires no special precautions in handling or in storage as do the methyl hydrogen polysiloxanes which tend to release hydrogen on standing.

A known method employs for the purpose of rendering leather water-repellent, a mixture of ingredients comprising a titanate, a methylpolysiloxane copolymer composed of trimethylsiloxy units and  $\text{SiO}_2$  units, and an organopolysiloxane containing from 2 to 2.9 organic radicals per silicon atom in which the organic radicals are selected from alkyl radicals, alkenyl radicals and monocyclic aryl radicals, i.e., hydrocarbon radicals of the aryl type which are free of substitution. However, we have found that prior known methylpolysiloxane compositions, such as those referred to above, when applied to textiles, for instance, cotton, fail to give any evidence of satisfactory water-repellency on the cotton, and in most cases the spray rating using such polysiloxane materials is zero. Even if such organopolysiloxanes contain both methyl groups and unsubstituted phenyl groups, the spray rating, for instance, on cotton, is erratic and much lower than the spray ratings obtainable by using the compositions of the present invention.

It is, therefore, one of the objects of this invention to obtain good water-repellency on textiles without requiring elaborate means of application of the water-repellent.

It is another object of the invention to render textile surfaces, such as cotton, rayon, acetate and nylon, water-repellent by convenient means without requiring heat to bring out the optimum water-repellency.

It is a still further object of the invention to render surfaces of garments water-repellent by means of convenient containers capable of being economically and practically used at home without requiring complicated equipment or specialized conditions for application.

Other objects of the invention will become more apparent from the following description thereof.

All the foregoing objects and desirable results are attained by employing in the water-repellent treating composition a mixture of ingredients in certain proportions comprising the aforesaid organotitanate, the methylpolysiloxane copolymer consisting essentially of trimethylsiloxy units and  $\text{SiO}_2$  units, and a methyl chlorophenylpolysiloxane more particularly described above. This mixture of ingredients is conveniently applied from an aerosol container from which the water-repellent composition is expelled onto the surface it is desired to treat by means of gaseous propellents in the form of a mist or spray of fine particles, wherein the propellent is a liquefied gas having a vapour pressure at room temperature ( $27^\circ \text{C}$ .) sufficiently high

to vaporize rapidly at room temperature and to propel the water-repellent composition onto the surface being rendered water-repellent.

The methylpolysiloxane resinous copolymer consisting essentially of trimethylsiloxy units and  $\text{SiO}_2$  units (hereinafter referred to as "methylpolysiloxane copolymer") may be prepared by various means. One method comprises cohydrolyzing a compound having the formula  $(\text{CH}_3)_3\text{SiX}$  with a compound having the formula  $\text{SiX}_4$ , where X is a hydrolyzable radical, e.g., chlorine, bromine, fluorine or an alkoxy (e.g., methoxy or ethoxy) radical, or an acyloxy radical, employing such proportions of ingredients as are necessary to obtain the desired methyl/Si ratio of from 1 to 1.25 methyl radicals per silicon atom. Instead of employing with the trimethyl hydrolyzable silane, monomeric tetrahydrolyzable silanes of the formula  $\text{SiX}_4$ , mentioned before, one can also employ polymeric alkyl silicates derived from controlled hydrolysis of the monomeric orthosilicate, wherein the polymeric alkyl silicate composition contains some silicon-bonded hydroxy groups.

The methylpolysiloxane copolymer is advantageously prepared by effecting cohydrolysis of the trialkyl hydrolyzable silane and an alkyl silicate (this designation for the silicate is intended hereinafter to include both the monomeric and polymeric forms of the alkyl silicate) by adding the trialkyl hydrolyzable silane and the alkyl silicate to a suitable solvent, such as toluene, benzene or xylene, and thereafter adding the solution of the ingredients to a sufficient amount of water to effect the desired hydrolysis and co-condensation in a suitably acidic medium. The choice of the solvent will depend on such considerations as, for instance, the particular trialkyl hydrolyzable silane and alkyl silicate used, the relative proportions of the ingredients, and the effect of the solvent on processing the hydrolysis and co-condensation product. In this respect, water-miscible solvents such as alcohols, ketones and esters, should be avoided since these materials do not effect adequate separation between the hydrolysis product and the water of hydrolysis so as to give satisfactory recovery of the reaction product of the trialkyl hydrolyzable silane and the alkyl silicate. The amount of solvent used may be varied widely but advantageously, by weight, it is within the range of from about 0.25 to 2 parts solvent per part of cohydrolyzate, that is, the trialkyl hydrolyzable silane and the alkyl silicate.

The amount of water used for hydrolysis purposes is generally not critical and may be varied within wide ranges. The minimum amount of water required is that necessary to hydrolyze all the silicon-bonded hydrolyzable radicals in the trialkyl hydrolyzable silane and all the alkoxy radicals in the alkyl silicate. The



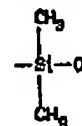
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maximum amount of water will generally be determined by the ease with which the co-hydrolyzate can be processed to isolate the co-hydrolysis product or resin. The amount of water used should be at least from 2 to 3 mols water per total molar concentration of the trialkyl hydrolyzable silane and the alkyl silicate. In general, the amount of water used should be as low as possible to assist in good yields of the methylpolysiloxane copolymer resin, while utilizing to the fullest extent the space available in equipment used for hydrolysis purposes. An upper range of water which may be used with satisfactory results is that of the order of about 40 to 50 mols per mol of the mixture of trialkyl hydrolyzable silane and alkyl silicate. For each mol of the trialkyl hydrolyzable silane, we preferably use from 1 to 2 mols of the alkyl silicate, advantageously within the range of from about 1.2 to 1.8 mols of the alkyl silicate per mol of trialkyl hydrolyzable silane. In the preparation of the resin, one may add up to 25 per cent, by weight, preferably from 3 to 15 per cent, by weight, based on the weight of the trialkyl hydrolyzable silane, of other cohydrolyzable materials, such as dimethyldiethoxysilane, dimethyldichlorosilane, diphenyldichlorosilane, methyl phenyldichlorosilane and methyltrichlorosilane to give difunctional or trifunctional siloxy units of the formula  $(R^{11})_2SiO$  and  $R^{11}SiO_{1/2}$ , where  $R^{11}$  is a monovalent hydrocarbon radical, e.g., methyl, ethyl, butyl, decyl, phenyl or benzyl radical. However, satisfactory properties in the material are often realized without these additional difunctional or trifunctional units and may be omitted if desired.

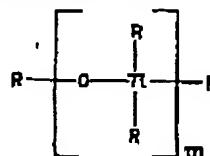
In preparing the resin, the trialkyl hydrolyzable silane and alkyl silicate are dissolved in a suitable solvent, and added with stirring to the water of hydrolysis, advantageously using temperatures of from 60° C. to 85° C. Thereafter, the two-phase system thus obtained is processed to remove the water-alcohol layer and the remaining resinous material is neutralized with a sufficient amount of sodium bicarbonate or other alkaline material to give the resin a pH of at least about 6 or 7. Thereafter, the resin is filtered and advantageously adjusted to a resinous solids content of about 30 to 65 per cent, using, where necessary, additional amounts of solvent such as toluene or xylene, in order to avoid premature gelation of the resin and to maintain its stability for a time sufficient to permit use with the other ingredients.

The presence of dimethylsiloxy units of the formula



intercondensed with the methylpolysiloxane copolymer is not precluded. Thus, in addition to trimethylsiloxy units and  $SiO_2$  units, one can have intercondensed dimethylsiloxy units which can be obtained by cohydrolyzing trimethylchlorosilane, an alkyl silicate, e.g., ethyl silicate, and dimethyldichlorosilane in which the latter is present in an amount ranging up to 25 weight per cent of the weight of the trialkyl hydrolyzable silane used to make the methylpolysiloxane copolymer.

The titanium compound suitable for employment in the composition of this invention may be monomeric orthotitanates of the formula  $(RO)_4Ti$  or polymers of the orthotitanate having the formula



where R is an alkyl radical which may be saturated or unsaturated and includes methyl, ethyl, propyl, butyl, decyl, undecyl, lauryl, palmityl and oleyl radicals, and m is an integer greater than 1. Preferably, R is an alkyl radical containing from 3 to 10 carbon atoms. The alkyl radicals on the oxygen attached to titanium may also have attached thereto hydroxyl or amino radicals so that the titanate contains hydroxylated or amino-substituted aliphatic hydrocarbon radicals. Among such titanium esters may be mentioned, for instance, tetramethyl titanate, tetraethyl titanate, tetrabutyl titanate, tetradecyl titanate, octylene glycol titanate, tetradodecyl titanate, tetra-(hydroxyethyl) titanate, tetra-(hydroxybutyl) titanate, tetra-(amino-ethyl) titanate and tetra-(methyl-aminobutyl) titanate. Titanium esters wherein R is the same or mixed radicals are likewise suitable.

Partially hydrolyzed compounds of the aforesaid class of orthotitanates obviously also may be used and preferably one employs particularly those partial hydrolyzates which are soluble in the solvents and the gaseous propellants which are to be used in the aerosol container. Additional examples of polymeric organotitanates which may also be used are,



e.g., polymers of tetraorgano derivatives of orthotitanic acid, including the tetra esters, tetra anhydrides, and tetra amides.

5 The lower alkyl chlorophenyl organopolysiloxane having the formula  $R^1_nSiO_{n-1}$ , where

the  $R^1$ 's are lower alkyl radicals (e.g., methyl and ethyl radicals) and chlorinated phenyl radicals, in which the chlorinated phenyl radicals contain an average of from 3 to 5 chlorine atoms per phenyl nucleus and the chlorinated phenyl radicals constitute from 5 to 25 per cent of the total number of lower alkyl and chlorophenyl radicals, and  $n$  has an average value of above 1.96 and below 2.5, may be prepared by various methods. One method for preparing these compounds comprises cohydrolyzing, in the proper proportions, trimethylchlorosilane, dimethyldichlorosilane (or diethyldichlorosilane), and chlorinated phenyltrichlorosilane. Thus, on a weight basis, one may employ from 1 to 9 per cent trimethylchlorosilane, from 75 to 95 per cent dimethyldichlorosilane, and from about 3 to 15 per cent chlorinated phenyltrichlorosilane. Alternatively, one may use mixtures of chlorosilanes in which the chlorophenyl radical attached to silicon has a methyl or radical attached directly to the same silicon, for instance, methyl trichlorophenyldichlorosilane, methyl tetrachlorophenyldichlorosilane, methyl tetrachlorophenyldiethoxysilane and ethyl tetrachlorophenyldichlorosilane. Higher chlorinated phenylchlorosilanes or other hydrolyzable silanes, such as pentachlorophenyltrichlorosilane, may be used without departing from the scope of the invention. The presence of certain triorganosiloxane units such as trimethylsiloxy units, or monomethylsiloxy units, is not precluded. The proportions of the hydrolyzable ingredients should be such in making the lower alkyl chlorophenylpolysiloxane that the ratio of total lower alkyl radicals and chlorinated phenyl radicals ranges from above 1.96, preferably at least 1.98, to below 2.5 of these radicals per silicon atom, and the chlorinated phenyl radicals constitute from 5 to 25 per cent of the total number of lower alkyl and chlorophenyl radicals. For optimum use, as water-repellent, and in the form of an aerosol composition, the lower alkyl chlorophenylpolysiloxane liquid should have a viscosity of from 10 to 100,000 centistokes when

measured at 25° C.

It will, of course, be apparent to those skilled in the art that in addition to the methylchlorosilanes and ethylchlorosilanes described above, other hydrolyzable lower alkyl silanes containing hydrolyzable radicals other than the chlorine atom may be used. The presence of, for instance, methyltrichlorosilane or other lower alkyl trihydrolyzable silanes, or of trimethylchlorosilane or other trisubstituted lower alkyl monochlorosilanes in preparing the lower alkyl, e.g., methyl, chlorophenylpolysiloxane is not precluded, as long as the value of  $n$  remains substantially in the specified range.

The titanate, methylpolysiloxane, resinous copolymer and the lower alkyl chlorophenylpolysiloxane are advantageously mixed with a suitable solvent for the mixture of ingredients, for instance, a Stoddard solvent which is an aliphatic solvent, or mineral spirits, and thereafter combined with a liquefied gas which will be used as the propellant for the mixture of polysiloxanes and the titanate. These liquefied gases or propellants are volatile liquid carriers which are solvents for the ingredients mentioned above, specifically the titanate, the methylpolysiloxane copolymer, and the lower alkyl chlorophenylpolysiloxane. They normally have a vapour pressure at 70° F. exceeding 20 lb./sq. in. gauge and are able to induce expulsion of the above mixture of titanate and organopolysiloxanes in extremely small average particle size, preferably within the range of about 10 to 100 microns. These propellants are non-toxic, have a high flash point, and are non-inflammable. In general, they are chlorinated, fluorinated alkanes, examples of which are dichlorodifluoromethane, dichlorofluoromethane, chlorodifluoromethane, trichloromonofluoromethane and difluorodichloroethane. Obviously, mixtures of these chlorinated, fluorinated alkanes may also be employed to advantage.

In addition to the propellant, other solvents may be employed, for instance, the above-mentioned mineral spirit, acetone, chlorinated hydrocarbons (e.g., trichloroethylene and ethylene dichloride and others).

When employed in the form of an aerosol bomb mixture, the ingredients are advantageously present, by weight, in the following amounts:



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Alkyl titanate (which includes polymeric alkyl titanates)	0.5 to 5 parts
Methylpolysiloxane copolymer	0.5 to 5 parts
Lower alkyl chlorophenylpolysiloxane	0.5 to 5 parts
Non-propellant solvent (e.g., mineral spirits)	5 to 60 parts
Gaseous propellant	40 to 120 parts

We have unexpectedly discovered that even greater improvements in water-repellency may be obtained and better feel and hand of the treated textile realized if, in addition to the titanate, methylpolysiloxane copolymer and lower alkyl chlorophenylpolysiloxane, there is also incorporated in the mixture of ingredients a wax, particularly a solid paraffin wax, which is soluble in the solvent as well as in the liquefied propellant. Advantageously, the paraffin wax (or other wax which is used) is preferably present on a weight basis in an amount equal to from 10 to 100 per cent or more of the total weight of the alkyl titanate, the methylpolysiloxane copolymer, and the lower alkyl chlorophenylpolysiloxane. The term "paraffin wax" is intended to include waxes melting, for instance, from about 35° to 200° C. or higher, but which are soluble in the solvent used in dissolving the other ingredients, and preferably soluble as well in the liquefied propellant. These are generally high melting hydrocarbons which are constituents of petroleum. They may have the formula  $C_nH_{2n+2}$ , where  $n$  is, for instance, from 18 to 70, or even much higher. Other waxes may be employed, such as beeswax, synthetic hydrocarbon waxes, microcrystalline and oxidized microcrystalline waxes, ceresin wax, Japan wax, polyethylene oxide waxes and halogenated paraffins.

The spray ratings in the following illustrative examples were determined in accordance with the method set forth in the 1945 Yearbook of the American Association of Textile Chemists and Colorists, Volume 22, pages 229-233. A spray rating of 100 is indicative of a textile's ability to shed all drops of water which may have impinged on the surface of a textile upon slight shaking of the textile surface.

In order that the invention may be better understood, the following examples are given. All parts are by weight.

The compositions described in the following examples were tested for their water-repellency on textiles by placing them in aerosol bombs or pressure vessels having a pressure valve nozzle. Unless otherwise stated, the liquefied propellant gases employed were

composed of trichlorofluoromethane and dichlorodifluoromethane in equal parts by weight. In each instance, the cotton material (which was unmodified and untreated cotton cloth) being tested was sprayed evenly on the fabric from an aerosol spray container, and allowed to dry 24 hours before evaluation. Thereafter, each of the treated textile surfaces was then tested for spray ratings, employing the method described in the above-mentioned American Textile Colorist Method.

#### EXAMPLE 1.

A methylpolysiloxane copolymer was prepared by cohydrolyzing 22.4 weight per cent trimethylchlorosilane and 77.6 weight per cent tetrachethyl orthosilicate. The cohydrolysis was carried out in toluene so that the final cohydrolysis product comprised 47 per cent solids (in toluene) and the methyl/Si ratio was about 1.07. This polymer will hereinafter be referred to as an "MQ resin."

#### EXAMPLE 2.

A methyl chlorophenylpolysiloxane liquid of about 50 centistokes (when measured at 25° C.) was prepared by cohydrolyzing on a weight basis, 8.5 per cent trimethylchlorosilane, 82.5 per cent dimethyldichlorosilane, and 9 per cent tetrachlorophenyltrichlorosilane. The ratio of the total number of methyl and tetrachlorophenyl radicals to silicon was of the order of about 2.06. This linear methyl chlorophenylpolysiloxane liquid (chain-stopped with trimethylsiloxy units) will hereinafter be referred to as "Fluid I."

#### EXAMPLE 3.

Another methyl chlorophenylpolysiloxane liquid of about 300 centistokes (when measured at 25° C.) was prepared by cohydrolyzing on a weight basis, 1 per cent trimethylchlorosilane, 90 per cent dimethyldichlorosilane, and 9 per cent tetrachlorophenyltrichlorosilane. This polymer had a ratio of about 1.98 total methyl tetrachlorophenyl radicals per silicon atom. This polymer will hereinafter be referred to as "Fluid II."

Aerosol bomb formulations were prepared by placing in a suitable pressure vessel the following ingredients which were present, by weight, as follows, assuming the presence of all the ingredients.



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TABLE I

Ingredient	Parts
Tetrabutyl titanate	1.5
Methylpolysiloxane copolymer (as 47% solids toluene solution)	1.5
Methyl tetrachlorophenylsiloxane liquid	1.5
*Paraffin wax	4.0
Mineral spirits	40.0
Dichlorodifluoromethane and trichlorofluoromethane (equal parts)	80.00

\* The paraffin wax used had an amine melting point (AMP) of 133° F. and was a refined grade of petroleum wax manufactured and sold by Gulf Oil Corporation.

In some instances, one or more of the above ingredients were omitted from the aerosol container to determine the effect of such omission.

5 The following Table II shows the results of spray ratings determined on cotton fabrics in which various combinations of the tetrabutyltitanate, methylpolysiloxane copolymer, methyl tetrachlorophenyl siloxane liquid and

paraffin wax were the variables. Where liquids were used, their composition is described below the table. In all the aerosol compositions, the amounts of the mineral spirits and the propellents were constant. The letter "x" indicates the presence of the particular ingredient. 15

TABLE II

Test No.	Tetrabutyl Titanate	MQ Resin	Other Liquid	Paraffin Wax	Spray Rating on Cotton		
1	-	-	-	x	0	0	0
2	x	x	-	x	0	0	0
3	x	-	Fluid I	x	0	0	0
4	-	x	Fluid I	x	0	0	0
5	x	x	Fluid I	-	100	100	100
6	x	x	Fluid II	-	100	100	100
7	x	x	Fluid I	x	100	100	100
8	x	x	Fluid II	x	100	100	100
9	x	x	* Fluid III	-	Average of three tests — 65		



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TABLE II

Test No.	Tetrabutyl Titanate	MQ Resin	Other Liquid	Paraffin Wax	Spray Rating on Cotton		
10	x	x	<sup>b</sup> Fluid IV	-	90	80	95
<sup>c</sup> 11	Composition commercially available				Average of three tests — less than 50		
12	x	x	<sup>d</sup> Fluid V	-	80	80	90
13	x	x	<sup>e</sup> Fluid VI	-	80	80	70

<sup>a</sup> Fluid III was a linear methyl phenylpolysiloxane liquid of about 120 centistoke viscosity (at 25° C.) chain-stopped with trimethylsiloxy units and containing both methyl radicals and phenyl radicals connected directly to silicon in which the phenyl radicals were free of any substitution; this composition contained about 25 mol per cent phenyl radicals.

<sup>b</sup> Fluid IV was a methyl phenylpolysiloxane linear liquid of about 500 centistokes viscosity (at 25° C.) chain-stopped with trimethylsiloxy units in which the phenyl radicals were free of substitution; there were present about 40 mol per cent silicon-bonded phenyl radicals.

<sup>c</sup> This composition, the proportions of whose ingredients were not exactly known, is sold commercially as a mixture comprising the above-mentioned MQ resin, tetrabutyl titanate, and a linear methylpolysiloxane liquid chain-stopped with trimethylsiloxy units and containing only methyl radicals in the linear polysiloxane chain; this composition was made up into an aerosol composition similarly as was done with the others.

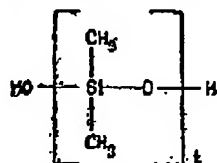
<sup>d</sup> Fluid V is a methyl hydrogen polysiloxane liquid of about 25 centistoke viscosity (at 25° C.) chain-stopped with trimethylsiloxy units and containing intermediate

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{---Si---O---} \\ | \\ \text{H} \end{array}$  units; such compounds are more particularly described in Specification No. 630,911.

<sup>e</sup> Fluid VI is a mixture of 60 parts of Fluid V and 40 parts of a trimethylsiloxy chain-stopped linear methyl polysiloxane of about 25 centistoke viscosity (at 25° C.) containing for the most part dimethylsiloxy units and a small percentage of monomethylsiloxy units ( $\text{CH}_3\text{SiO}_2/\text{a}$ ).

## EXAMPLE 4.

For this example, a methylpolysiloxane polymer composed of 1.0 mol trimethylsiloxy units and 108 mols  $\text{SiO}_2$  units, prepared similarly as in Example 1 above, was interacted with a linear polydimethylsiloxane liquid of about 200,000 centipoises viscosity when measured at 145° C., containing terminal silicon-bonded hydroxy units (the said polydimethylsiloxane having the formula



where  $t$  is an integer greater than 1). The weight ratio of the reactants was 75 per cent of the former and 25 per cent, by weight, of the polydimethylsiloxane. The reaction pro-

duct was now composed of intercondensed trimethylsiloxy units, dimethylsiloxy units, and  $\text{SiO}_2$  units. This copolymer (hereinafter identified as "MDQ polymer") was made into a water-repellent formulation composed of the following ingredients in the stipulated parts by weight.

Ingredients	Parts	
Tetrabutyltitanate	9.0	25
MDQ polymer	5.5	
Fluid I	5	30
Paraffin wax	9	
Xylene	30	
Mineral spirits	72	
Trichlorofluoromethane	88	
Dichlorodifluoromethane	132	

Aerosol bombs were prepared from the above mixture of ingredients and applied to cotton, viscose and acetate cloths by spraying the cloths and allowing them to dry at room temperature for about 16 hours. At the end of this time, the spray ratings of the three



cloths were determined and found to be an average of 100 for three samples of each of the treated cloths.

#### EXAMPLE 5.

- 5 In this example, another aerosol bomb mixture was prepared from the following ingredients:

	Ingredients	Parts
	Tetrabutyl titanate	9
10	MDQ polymer	6.3
	Fluid I	2.7
	Paraffin	9
	Mineral spirits	102
	Trichlorofluoromethane	84
15	Dichlorodifluoromethane	126

- Rayon gabardine of shades varying from tan to dark brown were sprayed with the above-identified formulation and allowed to air dry for about 16 hours at room temperature. Samples of these materials (which had spray ratings of around 100) were dry cleaned as well as were other samples of the cloth treated with a trimethylsiloxy chain-stopped methyl hydrogen polysiloxane such as Fluid V containing a catalyst and heat cured, were dry cleaned and the spray ratings again determined. The samples treated with the methyl hydrogen polysiloxane showed spray ratings of zero with the exception of the dark brown samples which had a spray rating of about 70. In contrast to this, the rayon gabardine samples sprayed and dried at room temperature in accordance with our invention all showed ratings of 70 or above after the spray ratings.

- It has been found that on dark fabrics, there may be a tendency for the paraffin or other waxes which may be employed to cause a slight haze on dark coloured fabrics. This tendency toward haziness can be materially reduced and often completely eliminated by incorporating in the aerosol mixture small amounts of such materials as stearic acid or glyceryl monostearate usually in amounts ranging from about 0.5 to 8 per cent, by weight, based on the total weight of the ingredients in the aerosol bomb container. Stated alternatively based on the mixture of the organic titanate, the methylpolysiloxane copolymer and the lower alkyl chlorinated phenyl polysiloxane, we can advantageously employ from about 5 to 30 per cent, by weight, of these anti-haze ingredients. As an additional advantage of these anti-haze ingredients, freezing or crystallizing out of the wax at the discharge orifice of the aerosol valve is essentially eliminated.

- The compositions containing wax in combination with butyl titanate, the methylpolysiloxane copolymer, and the methyl chlorophenylpolysiloxane materially improved the feel of the treated product and, as will be

noted above, did not harm the water-repellency. The improvement in feel of the treated cotton fabric was evidenced by a reduction in the slight tackiness of the fabric without the wax present thereon and a material softening of the surface of the treated fabric.

#### WHAT WE CLAIM IS:—

1. A composition comprising, by weight, (1) from 10 to 60 per cent of an orthotitanate having the general formula  $Ti(OR)_4$ , where each R is an aliphatic hydrocarbon radical of less than 12 carbon atoms or an hydroxylated or aminated aliphatic hydrocarbon radical of less than 12 carbon atoms and containing less than four hydroxy radicals, or an aliphatic hydrocarbon - soluble partial hydrolyzate thereof; (2) from 25 to 75 per cent of a methylpolysiloxane copolymer consisting essentially of trimethylsiloxy units and  $SiO_2$  units wherein said units are in such proportion that the ratio of methyl radicals to silicon atoms ranges from about 1 to 1.25 methyl radicals per silicon atom, and (3) from 10 to 50 per cent of a liquid organopolysiloxane having the formula  $R'_nSiO_{2-n}$  where

the  $R'$ 's represent both lower alkyl and chlorinated phenyl radicals in which the chlorinated phenyl radicals contains an average of from 3 to 5 chlorine atoms per phenyl nucleus, and the chlorinated phenyl radicals constitute from 5 to 25 per cent of the total number of lower alkyl and chlorophenyl radicals, and n has an average value of between 1.96 to 2.5, the lower alkyl chlorophenylpolysiloxane liquid having a viscosity of from 10 to 100,000 centistokes when measured at 25° C.

2. A composition as claimed in Claim 1, wherein the methylpolysiloxane copolymer contains trimethylsiloxy units, dimethylsiloxy units and  $SiO_2$  units.

3. A composition as claimed in Claim 1 or in Claim 2, wherein the lower alkyl chlorophenylpolysiloxane is a methyl chlorophenylpolysiloxane.

4. A composition as claimed in any of Claims 1 to 3, including a wax.

5. A composition as claimed in Claim 4, wherein the wax is paraffin wax.

6. A composition as claimed in any of Claims 1 to 5, including a volatile carrier.

7. A composition as claimed in Claim 6, wherein the carrier is a fluorinated alkane.

8. A composition as claimed in any of Claims 1 to 7, wherein the titanium compound is tetrabutyl titanate.

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